* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the additive agent and separator for a nonaqueous electrolyte secondary battery with high safety under high performance and the hot environments at the time of overcharge.
[0002]
[Description of the Prior Art]There are a method of using the safeguard with which a nonaqueous electrolyte secondary battery roughly divides, and is incorporated as a method of maintaining safety under the hot environments at the time of overcharge, and a method of giving the overcharge-proof characteristic to the power generation element itself.
[0003]There are what is depended on a separator, and a thing to depend on a overcharge-proof additive agent among these as an example of the method of giving the overcharge-proof characteristic further to the power generation element itself.
[0004]As a role which a separator plays about the safety of a cell, although there is usually prevention from a short circuit between the cathode at the time and an anode, When battery temperature rises remarkably according to the excess current by an external short circuit, etc. with a porosity polyolefin separator as a function peculiar to the separator of a nonaqueous electrolyte secondary battery, When a porous separator softens, there is what is called a shutdown function carried out by becoming quality of nonporous substantially and not making current send.
[0005]If the temperature of a cell rises, a separator will carry out melting even of after a shutdown, a hole will open it greatly, and between a cathode and an anode will short-circuit it (meltdown is called below). It can be said that the one of safety where the temperature at this time is higher is high. In order to strengthen a shutdown function, if thermal fusibility is improved, meltdown temperature will become low, and safety has the conflicting phenomenon of falling conversely.
[0006]Next, although some roles which a overcharge-proof additive agent plays are various, For example, when an additive agent polymerizes at the time of overcharge, internal resistance of a cell is made high, A conductive polymer is generated at the time of the method and overcharge abuse which generate gas at the time of the method of protecting a cell from a surcharge, or overcharge, and operate internal electroscission equipment certainly with predetermined internal pressure, and there are the method of making generate a short circuit and making it discharge automatically inside a cell, etc.

[0007]By development competition in recent years, the nonaqueous electrolyte secondary battery serves as high capacity increasingly. This high capacity-ization is performed on battery construction by lessening capacity of components other than an active material, and increasing quantity of the substantial active material in a cell, although there is also a field made highly efficient by improvement of the active material of an electrode. Therefore, the charge collector and separator of positive and negative poles aim to become increasingly thin. If a separator becomes thin, the safety to a short circuit etc. will aim to worsen, and also since the quantity of a substantial active material increases, the demand to safety becomes still larger.

[0008]Therefore, under the hot environments at the time of overcharge when a thin separator is used, not the method of only stopping a surcharge but the method of canceling an overcharging condition is effective. Speaking concretely, from the method of the internal resistance of a cell becoming high, generating gas by the method of protecting a cell from a surcharge at the time of overcharge, and operating internal electroscission equipment with predetermined internal pressure when an additive agent polymerizes by the above-mentioned method at the time of the shutdown of a separator, or overcharge of an additive agent etc. The method of making generate a short circuit situation and making it discharge automatically inside a cell is preferred.

[0009]However, when an aromatic additive is used for an additive agent, each time the same additive agent more, As indicated to JP,3061756,B, JP,3061759,B, and JP,H10-321258,A, When an additive agent polymerizes at the time of overcharge, internal resistance of a cell is made high, at the time of the method of protecting a cell from a surcharge, the method of operating the internal electroscission equipment which generates gas at the time of overcharge and operates with predetermined internal pressure, and overcharge abuse, a conductive polymer is generated and the operation which makes it discharge automatically is intermingled. For this reason, before canceling an overcharging condition by automatic discharge, it is SUBJECT that it is difficult for internal resistance to go up, or for generation of a conductive polymer to be barred by the generation of gas, and to secure safety by an internal short circuit certainly.

[0010]

[Problem to be solved by the invention]By this invention's solving above-mentioned SUBJECT and using it combining an additive agent and a suitable separator, safety is certainly secured by an internal short circuit, and it aims at providing the high capacity nonaqueous electrolyte secondary battery excellent in the safety under hot environments.

[0011]

[Means for solving problem]In order to solve above-mentioned SUBJECT, the cell of this invention polymerizes in the cell voltage exceeding peak operating voltage at the time of overcharge abuse, and serves as polymer, If voltage furthermore becomes high, said a part of polymer will oxidize, and it has positive charge, And a conductive polymer is generated when the negative ion in said nonaqueous electrolyte is doped by the positive charge part, the aromatic additive which has the operation which generates an internal short circuit is mixed by nonaqueous electrolyte -- the hole of per the unit area (square micrometer) of a separator -- it is characterized by a number being 100 or less.

[0012]By combining a separator with an aromatic additive and the characteristics parameter of these above-mentioned, the conductive polymer which polymerized at the time of overcharge penetrates a separator, an internal short circuit happens, and the nonaqueous electrolyte secondary battery of this invention cancels an overcharging condition. Therefore, it becomes possible to provide the nonaqueous electrolyte secondary

battery which was excellent in reliability with high capacity.

[0013]

[Mode for carrying out the invention]In the nonaqueous electrolyte secondary battery with which the nonaqueous electrolyte secondary battery of this invention was provided with the separator which consists of a cathode, an anode, nonaqueous electrolyte that dissolved electrolyte salt in the nonaqueous solvent, and porosity polyolefine, At the time of overcharge abuse, polymerize in the cell voltage exceeding peak operating voltage, and it becomes polymerization nature polymer, A conductive polymer is generated when said conductive polymer incorporates the lithium which furthermore deposited by the surcharge, The aromatic additive which has the operation which generates an internal short circuit is mixed by nonaqueous electrolyte, and said separator, using the value tau which calculated the rate tau of a curved road and was further calculated from using the electrical resistance Rm measured using the alternating-current-resistance measuring method (several 3) -- further (several 4) -- from -- the hole of calculated per an unit area (square micrometer) -- it is characterized by a number being 100 or less.

[0014]

[Mathematical formula 3]

$$\tau = \sqrt{\frac{S \cdot \varepsilon \cdot R_m}{\rho \cdot L}}$$

[0015](However, the void content and L in which the measuring-plane product calculated S and rho calculated the specific resistance of a measurement electrolysis solution and epsilon from the volume and weight of the separator are the thickness of a separator.)

[0016]

[Mathematical formula 4]

$$n/S = \frac{\varepsilon}{\pi (\frac{d}{2})^2 \cdot \tau}$$

[0017](However, it is the average pore size which measured the void content and pi which calculated epsilon from the volume and weight of the separator by the circular constant, and measured d by the mercury-porosimetry method.)

Although the cathode in this invention is conventionally publicly known composition, lithium content multiple oxides, such as cobalt acid lithium, nickel acid lithium, and a manganese spinel, are used as an active material, and the mixture which mixed the conducting agent and the binding agent is coated and produced by the charge collector.

[0018]Although carbon, such as natural graphite and an artificial graphite, is mainly used for an active material, the anode in this invention, In addition, there are conventionally publicly known things, such as an alloy of the versatility which makes aluminum and aluminum a subject, a metallic oxide of the versatility which makes the tin oxide etc. the start, metal nitride, and the mixed mixture is coated and produced by the charge collector in the conducting agent and the binding agent as well as a cathode.

[0019]In nonaqueous electrolyte (henceforth an electrolysis solution), as a nonaqueous solvent, cyclic

carbonate, such as ethylene carbonate (EC) and propylene carbonate (PC). What mixed two or more sorts of chain carbonate, such as dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC), is preferred.

[0020]Although the electrolyte salt can use publicly known lithium salt conventionally, $LiPF_6$, $LiBF_4$, etc. are preferred.

[0021]By the additive agent in this invention polymerizing in the cell voltage exceeding peak operating voltage, and generating a conductive polymer, It is an additive agent which consists of aromatic compounds which generate an internal short circuit at the time of overcharge abuse, For example, hexaphenylbenzene, terphenyl, phenylpiperazine, Tetrahydroisoquinoline, phenylcyclohexane, triphenylbenzene, Dodecahydronalium triphenylene, divinylbenzene, dicyclohexyl benzene, Biphenyl, pyrrole, N **MECHIRU pyrrole, a thiophene, a franc, Indore, a chlorothiophene, a bromothiophene, a fluorothiophene, Dimethoxy ** NZEN, a methylpyridinium tetrafluoro baud rate, diphenyl ether, benzofuran, diaryl ether, allylbutyl ether, phenoxytoluene, terphenyl, methyl terphenyl, dimethyl terphenyl, etc. have these derivatives.

[0022]In this, diphenyl ether, phenylcyclohexane, terphenyl, biphenyl, a franc, thiophenes, and these derivatives are desirable. Specifically, there are biphenyl, pyrrole, N **MECHIRU pyrrole, a thiophene, a franc, Indore, 3-chlorothiophene, 3-bromothiophene, 3-fluorothiophene, 1,2 dimethoxy ** NZEN, a 1-methyl-3-pyridinium tetrafluoro baud rate, etc.

[0023]Also among these, the point of the polymerization potential of an additive agent and the stability under battery actuation to diphenyl ether, phenylcyclohexane, o-terphenyl, biphenyl, a franc, Indore, and 3-chlorothiophene are especially preferred.

[0024]It is a fine porous thin film of electronic insulation where the separator of this invention has the big degree of ion permeation and which has a moderate mechanical strength, As construction material, porosity polyolefines of polypropylene resin and polyethylene resin, such as what was independent or laminated these, mixing, a compounded thing, are used from the viewpoint of organic solvent-proof nature and hydrophobicity, and a point with a shutdown function.

[0025]Although the manufacturing method of porosity polyolefine is roughly divided and has two processes, a wet type and dry type, after all give a hole, it is extended with one axis or two axes, and is made into porosity. therefore -- although many one simple breakthrough does not necessarily exist -- an aperture, fine-pores course length, and a hole -- in order to specify a number, the model shown in drawing 1 is generally used. Although the hole of various sizes is actually vacant as for the porous separator 1 on the separator surface 2, it has specified fine-pores course length, the rate of a curved road, and the number of holes of an unit area hit, having assumed that there was the breakthrough 3 of the same size that makes those average pore sizes d an aperture.

[0026]That is, fine-pores course length is the length of the breakthrough 3, and if separator thickness 4 is set to L, the breakthrough course length can express tauL and will call this proportionality coefficient tau the rate of a curved road.

[0027]A porous separator is thoroughly dipped in an electrolysis solution, and measurement of this rate of a curved road is performed with an alternating-current-resistance measuring method. In this case, it can be assumed that the breakthrough 3 is in the state where all were filled by the electrolysis solution, and there is a conductor of the same form as the breakthrough 3. The electrical resistance Rm can be expressed with the product of the ratio of course length tauL of a breakthrough to the gross area of the breakthrough in the

measuring-plane product S, and the specific resistance rho of an electrolysis solution at this time. The gross area of a breakthrough becomes what total hole volume could express with the product (SLepsilon) of the measuring-plane product S, separator thickness L, and the void content epsilon, and broke this by course length tauL. Therefore, as shown in (several 5), Rm can be expressed if these are arranged.

[0028]
[Mathematical formula 5]

$$R_m = \rho \cdot \frac{\tau^2 L}{\varepsilon} \cdot \frac{1}{S}$$

[0029]this (several 5) -- if it changes and asks about the rate epsilon of a curved road (several 3), it will become.

[0030]the volume V of one breakthrough -- a circular constant -- pi -- carrying out (several 6) -- since it can express -- a hole -- when the number is set to n, total hole volume (SLepsilon) can be expressed with (several 7).

[0031]
[Mathematical formula 6]

$$V = \pi \left(\frac{d}{2}\right)^2 \cdot \tau L$$

[0032]
[Mathematical formula 7]

$$n \cdot \pi \left(\frac{d}{2}\right)^2 \cdot \tau L = S L \varepsilon$$

[0033]this (several 7) -- changing -- the hole per unit area -- if it asks about a number (n/S) (several 4), it will become.

[0034]The model that n holes of this average pore size d are vacant is convenient for explaining theoretically the physical properties of a separator -- the infiltration resistivity T can be shown like (several 8), for example using the rate tau of a curved road -- and, generally is used widely.

[0035]
[Mathematical formula 8]

$$T = C \cdot \frac{\tau^2 L}{\varepsilon d}$$

[0036]Here, C is a proportionality constant and it is 0.13 in general, for example with a polyethylene separator.

[0037]The mechanism of an internal short circuit with the aromatic additive and separator of this invention under the hot environments at the time of the overcharge in the cell of this invention is as follows in general.

[0038]If the voltage of a cell becomes more than peak operating voltage at the time of overcharge, an aromatic additive will polymerize and grow within a positive electrode surface or separator fine pores, and will form a polymer layer. This polymer layer will oxidize selectively, if voltage becomes high further, it has

positive charge, and when the negative ion in an electrolysis solution, for example, PF^{6-} etc., is doped by the positive charge part, it serves as a conductive polymer. If an overcharging condition furthermore progresses, lithium comes to deposit in an anode.

[0039]While the conductive polymer which polymerized within the surface of a cathode and the separator surface by the side of a cathode, or fine pores exists, if a surcharge advances, the lithium which deposited in the anode side will grow toward a cathode needlelike, and will reach a cathode finally, and an internal short circuit will happen. next -- in this operation -- the hole of per the unit area (square micrometer) of a suitable separator -- a number exists. As for this Reason, the sludge (henceforth a dendrite) by the side of an anode grows like lightning needlelike independently with the pole diameter d and the rate tau of a curved road of the separator. It is important to centralize a dendrite for causing an internal short circuit in the early stage of a surcharge, and to tie with the conductive polymer in fine pores, and it becomes correlation with the number of holes of the breakthrough of a separator. That is, the number of holes of an unit area hit is a parameter which is technically meaningful.

[0040]the separator in this invention -- the hole of per an unit area (square micrometer) -- a number is 100 or less. this hole -- since time until a conductive polymer penetrates a separator and reaches a cathode is taken and a surcharge advances when a number is 101 or more, it becomes a dangerous situation. therefore, the hole of above-mentioned per an unit area (square micrometer) -- it is preferred that a number is 100 or less.

[0041]As a result, in the cell using the separator of this invention, a state with too much charge depth more than needed of a cathode and an anode is not reached from the comparatively early stage of a overcharge process, but the danger at the time of overcharge can be controlled.

[0042]In this operation, even if the aromatic additive is not added or it is carried out, less than 0.1weight % of a case will advance to a state with a dangerous overcharging condition, before a conductive polymer grows enough.

[0043]When larger [there are many aromatic additive additions, and], for example than 10 weight %, the depressor effect of an overcharging condition is incongruent since the usual battery characteristic, especially the characteristic at the time of high temperature preservation deteriorate, although it can demonstrate.

[0044]By combining a separator with an aromatic additive and the characteristics parameter of these above-mentioned, at the time of overcharge, a separator is penetrated, an internal short circuit happens and an overcharging condition is canceled by the conductive polymer which polymerized. Therefore, it becomes possible to provide the nonaqueous electrolyte secondary battery which was excellent in reliability with high capacity.

[0045]the hole of per the unit area (square micrometer), this invention persons, -- the separator with the following characteristic obtained wholeheartedly Conclusion of being suitable for the cell of this invention, as a result of examination from the infiltration resistivity for satisfying the usual battery capacity, the void content, the average pore size, the rate of a curved road, etc., securing a number. An aromatic additive especially Diphenyl ether, phenylcyclohexane, When it is what is chosen from the group which consists of o-terphenyl, biphenyl, a franc, Indore, and a 3-chlorothiophene at least one, although the number of holes of an unit area hit of said separator is 50 or less, the dramatically outstanding effect is shown.

[0046]Since the infiltration resistivity of a separator becomes disadvantageous [in respect of battery characteristics, such as efficient discharge of a cell,] in 460 seconds/100 ml or more, it is preferred that it is

preferred that it is 450 or less seconds/100 ml, and a void content is not less than 30% in a similar manner at least 29% or less since it is disadvantageous in respect of a battery characteristic. Since thickness not only becomes disadvantageous in not less than 31 micrometers in respect of battery characteristics, such as high-capacity-izing of a cell, and but high rate discharge, but an internal short circuit becomes difficult to happen, 30 micrometers or less are preferred. If thickness is set to 7 micrometers or less, even if an internal short circuit will occur certainly under the hot environments at the time of overcharge, a cell becomes a dangerous situation for thinness. Therefore, it is preferred that the thickness of a separator is 8 to 30 micrometers. however, the hole of per the unit area (square micrometer) for securing property values with which it is usually satisfied of the battery characteristic in the range, such as infiltration resistivity, a void content, thickness, and the safety at the time of overcharge -- the property value for securing a number has the conflicting relation. It is preferred that an average pore size is 0.06 micrometers or more as common physical properties with which it is satisfied of these both.

[0047]Here, each measuring method of the separator characteristic described above is explained below.

[0048]Although there are various measuring methods, such as the method of computing an average pore size using a fluid penetration method about a pole diameter, a method of detecting the maximum aperture using the bubble point method, the method of computing an average pore size using a method of mercury penetration, and a method of observing the diameter of a surface hole from a SEM surface photograph, With a measuring method, these values cannot necessarily be in agreement and cannot be compared using the value from which a measuring method is different. Then, inventors adopted the average pore size d measured from the method of mercury penetration.

[0049]About the infiltration resistivity T, the measuring method specified by JIS P8117-1998 was adopted.

[0050]The electrical resistance Rm dipped the separator in the electrolysis solution thoroughly, sandwiched it with the stainless board with the area of 2.54 cm^2, and was measured by the alternating-current-resistance measuring method. It measured on the occasion of alternating-current-resistance measurement, scanning a test frequency sequentially, and the value which crosses a real number axis was made into the electrical resistance Rm. Although frequency is an infinite value theoretically, in polyethylene monolayer, this value is 100 kHz and becomes almost the same as that of this value.

[0051]The void content epsilon calculated apparent specific gravity from the volume and weight of the separator, and asked for it from the difference from true specific gravity.

[0052]

[Working example]Next, the example of this invention is explained using working example.

[0053]First, the separator measured many polyethylene monolayer separators and extracted the separator with various kinds of characteristics described below.

[0054]In <extraction of separator> this example, the polyethylene monolayer separator with a thickness of 16 micrometers which has the following characteristics as the separator A was chosen.

[0055]The average pore size d measured with the method of mercury penetration was 0.075 micrometer, and the void content epsilon was 40%.

[0056]In electric resistance measurement, what dissolved 1 mol/l. $LiPF_6$ in the mixed solvent of the volume ratio 1:1 of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) was used for the electrolysis solution. The specific resistance rho of this electrolysis solution is 116-ohmcm. The electrical resistance Rm

was 0.738ohm.

[0057]the hole of per an unit area (square micrometer) which the rate tau of a curved road for which it asked using this Rm value (several 3) was 2.01, and assigned this value to (several 4) and calculated it further -- the number was 45 pieces.

[0058]Infiltration resistivity was measured using A type measuring device based on JIS in the laboratory by which temperature control was finally carried out to 23 **. The infiltration resistivity T was 310 seconds/100 ml. Hereafter, 13 sorts of separators of N were selected out of the separator A of a property value as shown in (Table 1) by the same method as the separator A.

[0059]

[Table 1]

セパレータ	透気抵抗度 (sec/100cc)	厚み (μm)	空孔率 (%)	平均孔径 (μm)	単位面積当り 孔数
A	310	16	36	0.075	43
B	410	16	36	0.067	45
C	100	23	50	0.11	43
D	250	16	41	0.085	34
E	110	16	52	0.2	7
F	500	16	36	0.068	40
G	800	16	30	0.06	40
H	1100	16	28	0.06	33
I	1200	16	30	0.055	43
J	220	16	46	0.06	100
K	370	16	35	0.03	342
L	600	16	38	0.03	385
M	200	16	52	0.06	256
N	225	6	32	0.06	48

[0060]In order to evaluate the temperature change at the time of overcharge of the cell of <production of cell> this invention, the square-shaped cell explained below was produced.

[0061]Structural drawing (part sectional view) of the square-shaped cell of working example 1-34 of this invention is shown in drawing 2.

[0062]As for the nonaqueous electrolyte secondary battery 5, in drawing 2, the cathode 6, the anode 7, and the separator 8 are wound, it is built in the case 9 with the electrolysis solution (not shown) which dissolved electrolyte salt in the nonaqueous solvent, and is sealed with the obturation board 10, although it is and safety elements, such as a safety valve and a PTC element, are included in the obturation board in the common cylindrical battery, In the cell of working example, no security apparatus is included in the obturation board 10 for the square shape.

[0063]The cathode 6 mixes 5 weight % of polyvinylidene fluoride resin (PVdF resin) of 10 weight % and a binding agent to 85 weight % of cobalt-acid-lithium powder in the carbon powder end of a conducting agent, The drying NMP was made to distribute these and the slurry was produced, and it applied on the positive

pole collector which consists of aluminum foil, and it rolled after desiccation and produced.

[0064]5 weight % was mixed for PVdF resin of the binding agent, using artificial-graphite powder as negative electrode active material, to 95weight % of this, the drying NMP was made to distribute these, the slurry was produced, the anode 7 was applied on the negative pole collector which consists of copper foil, and it was rolled after desiccation and it produced it.

[0065]13 sorts of separators of N were used for the separator 8 from the separator A shown in the above-mentioned (table 1).

[0066]what was used for the electrolysis solution at measurement of the electrical resistance Rm -- the same -- what dissolved 1 mol/l. LiPF$_6$ in the mixed solvent of the volume ratio 1:1 of EC and EMC was used. The amount of electrolysis solutions is about 2.5 ml.

[0067]This produced square-shaped cell is 30 mm in width, 48 mm in height, and 5 mm in thickness. The design capacity of what is usually marketed in this size is 700mAh, and its 25 to 27-micrometer thing is [the thickness of the separator 8] common. The cell of this example made 750mAh of high capacity design capacity rather than it. For this reason, when the thickness of the separator 8 became larger than 25 micrometers, the wound group of electrode was not able to insert it in the case certainly.

[0068]The <working example 1> separator A was assembled on the cell with 2.5 ml of electrolysis solutions which added 5weight % of biphenyl. Let this cell be a cell of working example 1.

[0069]The aromatic additive was assembled on the cell with the added electrolysis solution using the separator A by the same method as <comparative example 1> working example 1.

[0070]Table 3 Hereafter, it combined with 13 sorts of separators of N like an aromatic additive and its addition (Table 2) from the separator A shown in the above-mentioned (table 1), and the cell of working example 2-101 and the comparative examples 2-9 was assembled.

[0071]<evaluation of a cell> -- the these-produced cell and the method of describing a total of 105 pieces below estimated.

[0072]The design capacity of a cell is 750 mA. First, it is 10 cycle ********** about the charging and discharging cycle discharged after charging until it is set to 4.2V by 380-mA constant current until it is set to 3.0V by 380-mA constant current. Service capacity of this 10 cycle eye was made into the initial capacity of each cell. Initial capacity was satisfied with all the 27 cells of design capacity. Charge and discharge were performed in a 20 ** thermostat. Then, each cell was charged by 380-mA constant current to 4.2V, and it discharged to 3.0V by 1500-mA constant current. It computed as a rate of 2C capacity factor by the capacity / initial capacity x100 at this time. The overcharge examination of 3 hours was done by 750 more-mA constant current, the skin temperature of the cell in this process was measured, and the highest arrival temperature of the cell was evaluated. These results are also shown in (Table 2).

[0073]

[Table 2]

電池	セパレータ	添加剤	添加量(重量%)	2C容量比率(%)	電池の到達温度(℃)
実施例1	A	ジフェニルエーテル	5	90	98
実施例2	B	ジフェニルエーテル	5	87	102
実施例3	C	ジフェニルエーテル	5	95	105
実施例4	D	ジフェニルエーテル	5	93	105
実施例5	E	ジフェニルエーテル	5	95	110
実施例6	F	ジフェニルエーテル	5	77	100
実施例7	G	ジフェニルエーテル	5	72	98
実施例8	H	ジフェニルエーテル	5	63	97
実施例9	I	ジフェニルエーテル	5	60	108
実施例10	J	ジフェニルエーテル	5	90	115
実施例11	A	ジフェニルエーテル	2.5	92	102
実施例12	B	ジフェニルエーテル	2.5	91	105
実施例13	C	ジフェニルエーテル	2.5	98	102
実施例14	D	ジフェニルエーテル	2.5	95	106
実施例15	E	ジフェニルエーテル	2.5	96	113
実施例16	F	ジフェニルエーテル	2.5	87	100
実施例17	G	ジフェニルエーテル	2.5	80	105
実施例18	H	ジフェニルエーテル	2.5	67	102
実施例18	I	ジフェニルエーテル	2.5	65	95
実施例19	J	ジフェニルエーテル	2.5	91	117
実施例20	A	フェニルシクロヘキサン	5	89	95
実施例21	B	フェニルシクロヘキサン	5	86	100
実施例22	C	フェニルシクロヘキサン	5	95	98
実施例23	D	フェニルシクロヘキサン	5	95	103
実施例24	E	フェニルシクロヘキサン	5	95	109
実施例25	F	フェニルシクロヘキサン	5	80	97
実施例26	G	フェニルシクロヘキサン	5	76	98
実施例27	H	フェニルシクロヘキサン	5	63	97
実施例28	I	フェニルシクロヘキサン	5	60	97
実施例29	J	フェニルシクロヘキサン	5	92	110
実施例30	A	フェニルシクロヘキサン	2.5	91	108
実施例31	B	フェニルシクロヘキサン	2.5	89	105
実施例32	C	フェニルシクロヘキサン	2.5	96	100
実施例33	D	フェニルシクロヘキサン	2.5	96	113
実施例34	E	フェニルシクロヘキサン	2.5	95	117
実施例35	F	フェニルシクロヘキサン	2.5	80	108
実施例36	G	フェニルシクロヘキサン	2.5	66	106
実施例37	H	フェニルシクロヘキサン	2.5	62	104
実施例38	I	フェニルシクロヘキサン	2.5	59	106
実施例39	A	o-ターフェニル	5	89	95
実施例40	B	o-ターフェニル	5	85	101
実施例41	C	o-ターフェニル	5	92	103
実施例42	D	o-ターフェニル	5	90	105
実施例43	E	o-ターフェニル	5	91	111
実施例44	F	o-ターフェニル	5	72	100
実施例45	G	o-ターフェニル	5	70	98
実施例46	H	o-ターフェニル	5	57	97
実施例47	I	o-ターフェニル	5	55	97
実施例48	J	o-ターフェニル	5	87	112
実施例49	A	o-ターフェニル	2.5	91	105
実施例50	B	o-ターフェニル	2.5	90	104
実施例51	C	o-ターフェニル	2.5	95	106
実施例52	D	o-ターフェニル	2.5	95	110
実施例53	E	o-ターフェニル	2.5	96	115
実施例54	F	o-ターフェニル	2.5	88	104
実施例55	G	o-ターフェニル	2.5	75	102
実施例56	H	o-ターフェニル	2.5	67	101
実施例57	I	o-ターフェニル	2.5	63	100
実施例58	J	o-ターフェニル	2.5	89	115
比較例1	A	なし	—	95	250以上
比較例2	K	ジフェニルエーテル	5	91	250以上
比較例3	L	ジフェニルエーテル	5	77	250以上
比較例4	M	ジフェニルエーテル	5	93	250以上
比較例5	N	ジフェニルエーテル	5	94	250以上
比較例6	K	ジフェニルエーテル	2.5	90	250以上
比較例7	L	ジフェニルエーテル	2.5	79	250以上
比較例8	M	ジフェニルエーテル	2.5	92	250以上
比較例9	N	ジフェニルエーテル	2.5	91	250以上

[0074]

[Table 3]

電池	セパレータ	添加剤	添加量（重量%）	2C容量比率(%)	電池の到達温度(℃)
実施例59	A	ビフェニル	5	89	95
実施例60	A	ビフェニル	2.5	92	100
実施例61	B	ビフェニル	5	89	98
実施例62	C	ビフェニル	5	93	105
実施例63	D	ビフェニル	5	94	101
実施例64	E	ビフェニル	5	93	110
実施例65	F	ビフェニル	5	82	98
実施例66	H	ビフェニル	5	67	97
実施例67	I	ビフェニル	5	60	97
実施例68	J	ビフェニル	5	90	112
実施例69	A	フラン	5	91	98
実施例70	A	フラン	2.5	92	99
実施例71	B	フラン	5	89	103
実施例72	C	フラン	5	95	105
実施例73	D	フラン	5	91	111
実施例74	E	フラン	5	92	99
実施例75	F	フラン	5	75	105
実施例76	G	フラン	5	67	103
実施例77	H	フラン	5	61	102
実施例78	I	フラン	5	61	104
実施例79	J	フラン	5	88	111
実施例80	A	インドール	5	92	94
実施例81	A	インドール	2.5	93	98
実施例82	B	インドール	5	87	109
実施例83	C	インドール	5	97	109
実施例84	D	インドール	5	95	98
実施例85	E	インドール	5	96	112
実施例86	F	インドール	5	81	104
実施例87	G	インドール	5	73	105
実施例88	H	インドール	5	70	108
実施例89	I	インドール	5	70	109
実施例90	J	インドール	5	91	115
実施例91	A	3-クロロ-チオフェン	5	91	96
実施例92	A	3-クロロ-チオフェン	2.5	93	98
実施例93	B	3-クロロ-チオフェン	5	90	109
実施例94	C	3-クロロ-チオフェン	5	98	111
実施例95	D	3-クロロ-チオフェン	5	95	98
実施例96	E	3-クロロ-チオフェン	5	96	115
実施例97	F	3-クロロ-チオフェン	5	77	110
実施例98	G	3-クロロ-チオフェン	5	64	109
実施例99	H	3-クロロ-チオフェン	5	60	109
実施例100	I	3-クロロ-チオフェン	5	60	96
実施例101	J	3-クロロ-チオフェン	5	95	112

[0075]By the cell of working example 1-58, it was not concerned that the separator is thin, either but the abnormal temperature rise was stopped as I understood from (Table 2). By the cell of all the working example, where voltage is built, current is flowing, and the minute internal short circuit had happened within the separator. The abnormal temperature rise all of the cell of the comparative examples 1-9 happened to it.

[0076]although all the used polar-plate sizes and the size of the ordinary temperature of a separator were the same, there were a cell by which an abnormal temperature rise happens like the cell of working example and a comparative example, and a cell not happening -- the above-mentioned passage -- the hole per unit area -- it is because a number is different.

[0077]Since [which is not] he would like to add an aromatic additive, the comparative example 1 is considered that the abnormal temperature rise happened.

[0078]and the cell (comparative examples 2, 3, 4, 6, 7, and 8) of the comparative example which uses the separator K, M, and L -- the hole per unit area -- since growth distributed since there were many numbers, and it did not result in the internal short circuit but the overcharging condition progressed to the dangerous state, it is thought that the abnormal temperature rise happened.

[0079]Since the thickness of an internal short circuit of what is carried out is small, intensity is extremely

weak, an internal short circuit generates too much many internal short circuits in ** to which the amniorrhexis of what is carried out happened, and since the cell (comparative example 9) of the comparative example which uses the separator N has the large rise in heat by a short-circuit current, it is considered that the abnormal temperature rise happened.

[0080]It is that whose addition is 2.5 weight % with all the additive agents of working example 1-101, and 5weight % of a thing, and there was no difference in an effect.

[0081]

[Effect of the Invention]In spite of having used the thin separator, according to this invention, the safety under the elevated-temperature situation of a nonaqueous electrolyte secondary battery can be improved as stated above.

[Translation done.]